

**NORTHERN CONTAMINANTS INTERLABORATORY  
QUALITY ASSURANCE PROGRAM**

**Yvonne D. Stokker**

**National Laboratory for Environmental Testing  
National Water Research Institute  
Burlington, Ontario L7R 4A6**

*presented at  
Arctic Monitoring & Assessment  
Program (AMAP) Conference  
TROMSØ Norway  
Jan 28-31, 2002.*

**January 2002**

**NWRI Contribution No. 03-xxx**

## ABSTRACT

Throughout Phase I and Phase II of Canada's Northern Contaminants Program (NCP), the quality and reliability of measurement data have been monitored by a series of interlaboratory quality assurance (QA) studies. These intercomparisons have assessed the precision, accuracy and comparability of results generated by the NCP measurement laboratories for organochlorinated pesticides (OCs), PCBs, dioxins/furans, PAHs, toxic heavy metals, methylmercury, organotins and toxaphene. Annual intercomparisons on heavy metals have shown that considerable confidence can be placed in the reliability of data generated for arsenic, cadmium, copper, mercury, selenium, zinc, methylmercury and total organic mercury. With few exceptions, OC and PCB data in biotic samples are generally accurate and comparable at concentrations greater than 1 ng/g. Also, the results for the NCP's first toxaphene intercomparison are very encouraging, particularly for congener-specific analyses. However, the wide-ranging results for total toxaphene call for more careful scrutiny of these data. Given these findings, future toxaphene studies will continue to evaluate both total toxaphene and congener-specific results and will address the intercomparability of toxaphene standards. Finally, this presentation compares the key findings of this on-going QA program with those of other international intercomparison programs.

# Northern Contaminants Interlaboratory Quality Assurance Program

## INTRODUCTION

The Northern Contaminants Quality Assurance (QA) Program provides information on the quality, reliability and comparability of measurement results produced by laboratories generating data for Canada's Northern Contaminants Program (NCP) research projects. This information assists NCP science managers and northerners to make informed decisions regarding the sources of contaminants and their effects on the Arctic environment and on human health. In addition, this information helps to ensure that the NCP's contributions to international agreements and controls to protect the health of the Arctic ecosystem and northerners are based on scientifically sound data. Specifically, this program ensures that contaminants' data produced in NCP laboratories are written with acceptable levels of precision and accuracy, and that there will be comparability of data among the different laboratories and between research projects.



**Figure 1.** Interlaboratory test samples.

## ACTIVITIES

At the onset of Phase II of the NCP, two surveys were conducted: the first to report on the analytical capabilities and program directions of NCP laboratories<sup>1</sup> and the second to assess the suitability of various external QA programs to complement the NCP's own program of intercomparison studies<sup>2</sup>. Biotic samples being analyzed in the various research studies were predominately fish, marine and terrestrial mammals, bird tissues and eggs, as well as human tissue samples, such as blood, urine, hair, adipose tissue and milk. On the abiotic side, test matrices included air, water, snow and sediment. Since it was determined that the quality of nutrient and radionuclide measurements, and analyses of human tissues and most environmental samples were being adequately addressed by other external programs, the immediate QA priorities of the NCP were deemed to be persistent organic pollutants, including organochlorine pesticides (OCs), PCBs and toxaphene, and heavy metals and methylmercury in biotic tissues. Table 1 lists the NCP Phase II intercomparison studies conducted from 1998 to the present. Most of the matrix samples used in these studies have been biotic tissues from the north. Some international certified reference materials (CRMs) have been included to assess accuracy, and the use of standard solutions allows for the inclusion of the abiotic testing laboratories in the program. (Figure 1 illustrates the mix of test samples used in a typical intercomparison study.) In each study, data were assessed for accuracy, precision and bias, and where possible, Z-scores were calculated.

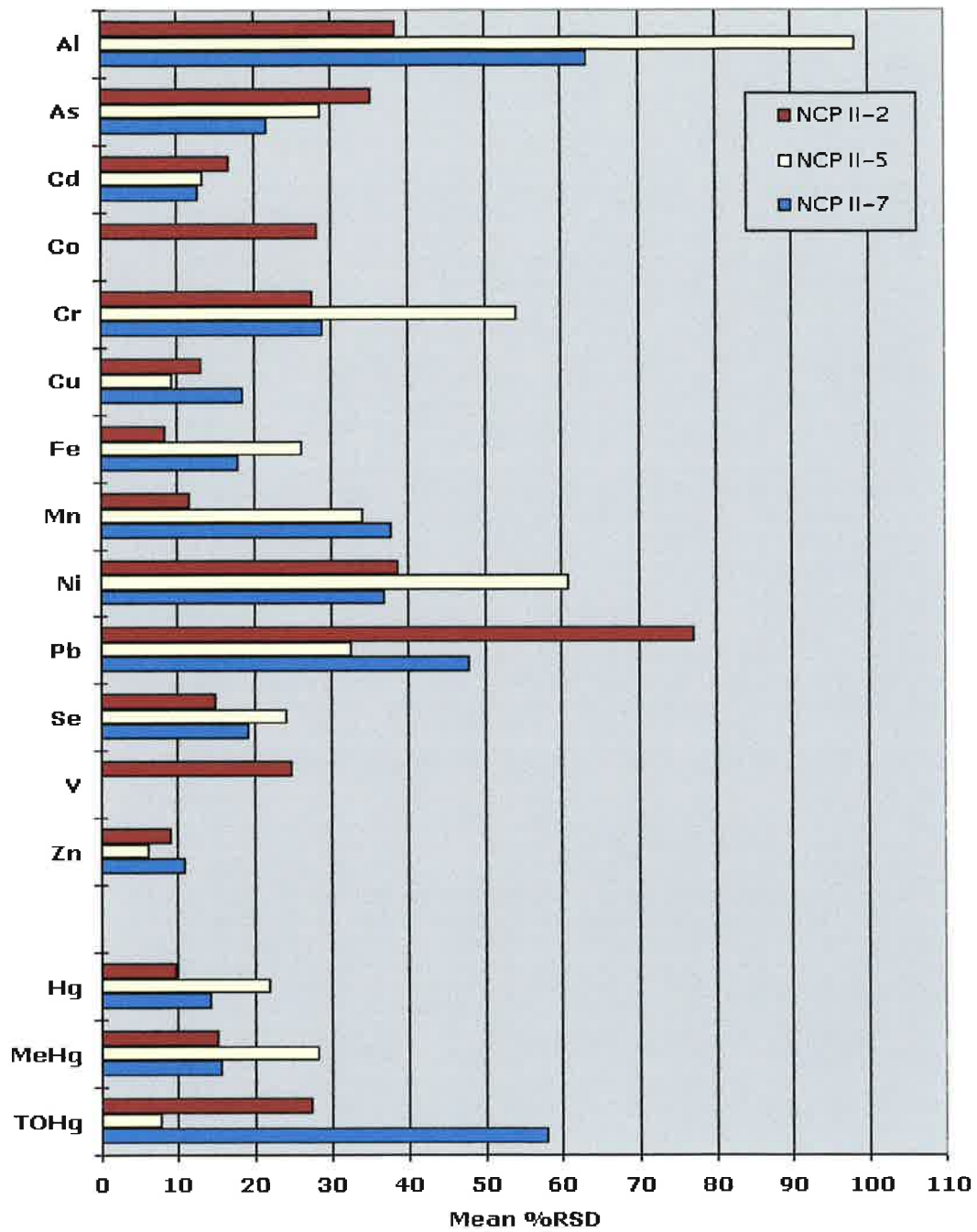
<b>Study No.</b>	<b>Target Analytes</b>	<b>Test Samples</b>	<b>Status</b>
<b>NCP II-1</b>	heavy metals	Great Lakes sediment CRMs	Complete
<b>NCP II-2</b>	heavy metals methylmercury total organic mercury	whole lake trout (Northern Québec) ringed seal muscle (Northern Québec) mussel homogenate CRM, fish muscle CRM	Complete
<b>NCP II-3</b>	21 organochlorines 30 PCB congeners 4 coplanar PCBs	standard solutions of OCs, PCBs and coplanar PCBs whole lake trout (Great Lakes) dried mussels CRM	Complete
<b>NCP II-4</b>	total toxaphene toxaphene congeners	technical toxaphene solutions (Hercules standard) mix of 13 toxaphene congeners lipid-free burbot liver (Yukon, Northwest Territories)	Complete
<b>NCP II-5</b>	heavy metals methylmercury total organic mercury	Narwhal muktuk (Nunavut) land-locked char filets (Nunavut) burbot liver (Yukon, Northwest Territories)	Complete
<b>NCP II-6</b>	organotins (specifically MBT, DBT and TBT)	standard solutions dried sediments, dried fish CRM, dried mussel CRM	Complete
<b>NCP II-7</b>	heavy metals methylmercury total organic mercury	caribou liver (Northwest Territories) ringed seal liver and kidney (Baffin Bay) Greenland shark muscle	In progress
<b>NCP II-8</b>	22 organochlorines 30 PCB congeners 12 WHO PCBs	mixed OC/PCB standard solution solution of 12 WHO PCB congeners polar bear blubber (Alaska), ringed seal blubber (Baffin Bay) Lake Ontario Coho salmon, Lake Superior siscowet	In progress
<b>NCP II-9</b>	total toxaphene homologue totals toxaphene congeners	technical toxaphene, mixture of 15 toxaphene congeners Lake Superior siscowet beluga whale blubber (Nunavut)	In progress
<b>NCP II-10</b>	heavy metals methylmercury	polar bear liver, seabird tissue, Northern Pike or walleye sediment	proposed for 2002
<b>NCP II-11</b>	toxaphene	technical toxaphene and congener mix solutions seal blubber, burbot liver extract	proposed for 2002

**Table 1. Interlaboratory studies conducted during Phase II of the NCP Quality Assurance Program.**

## KEY FINDINGS

### *Toxic Heavy Metals and Methylmercury:*

The reliability of heavy metal analyses has steadily improved over the four intercomparison studies but remains strongly metal dependant. In NCP II-1, the laboratories employing hydrofluoric acid (HF) in their digest procedure generated accurate and precise results for most of the heavy metals in the test sediments. However, significant losses of silicate minerals such as aluminum, chromium and vanadium were demonstrated by those who did not use HF. For metals in biota, laboratory performance was limited in many cases by the very low levels in the test samples. Nevertheless, as shown in Figure 2, the interlaboratory comparability was very good for toxic heavy metals such as arsenic, cadmium, copper, mercury, selenium and zinc, while aluminum, chromium and nickel data were less comparable among laboratories. Although bias for various metals was evident among all the participants at the onset of this QA program, it has improved considerably in the last two trace metal studies, with very few participants now exhibiting any metal bias. Methylmercury and total organic mercury data have generally been reliable throughout Phase II of the NCP, with the latter measurements being limited by their much higher detection limits.



**Figure 2.** *Relative standard deviations (%RSDs) of heavy metals and methylmercury for three intercomparison studies on Arctic biota samples. The test samples for NCP II-5 (muktuk, char and burbot liver) had very low concentrations of most metals.*

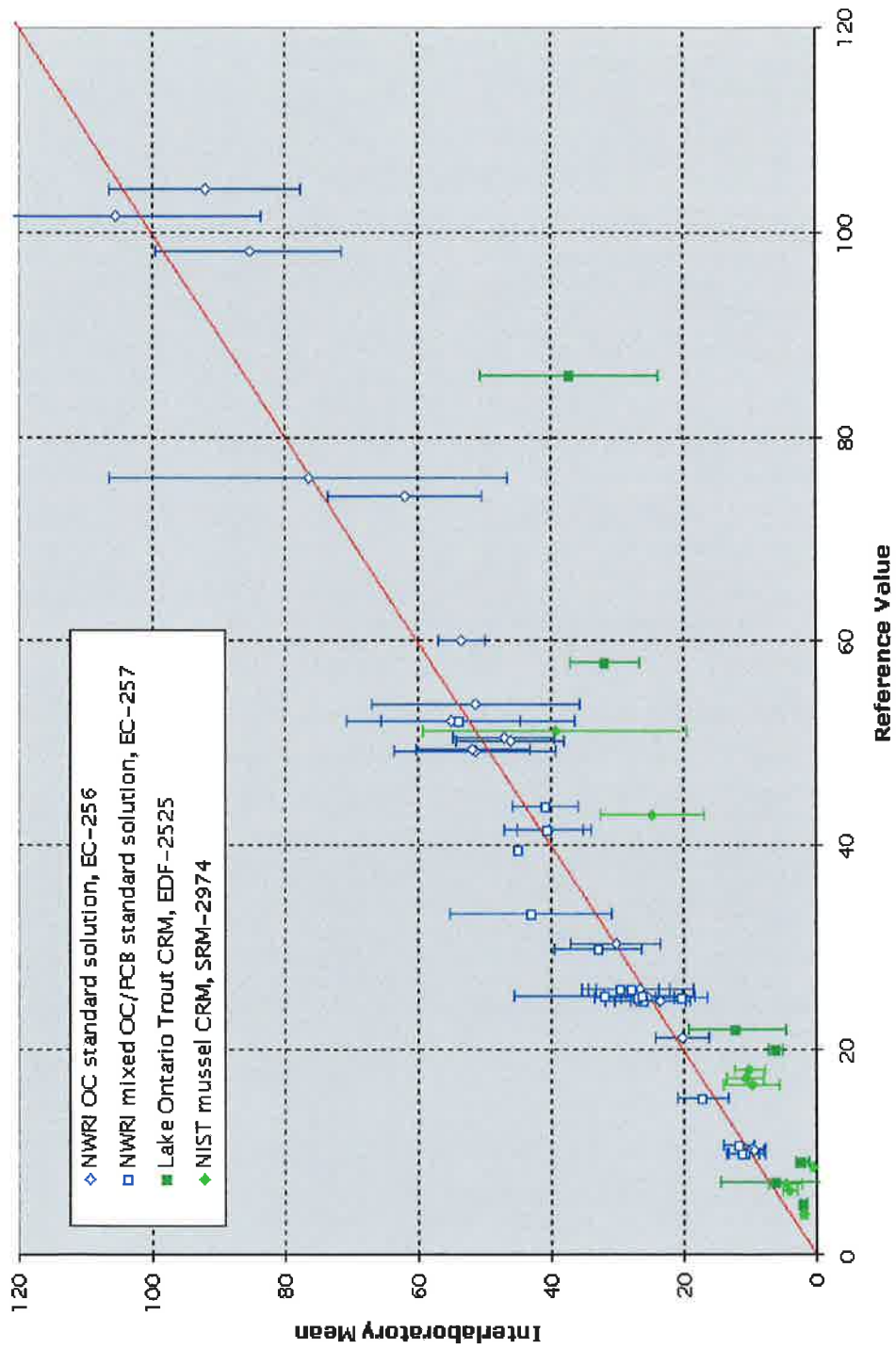
### ***OCs and PCBs:***

The analyses of 21 OCs and 30 PCB congeners in injection-ready solutions were generally quite accurate and comparable. This provides considerable confidence in the quality of calibration solutions being used. However, as shown in Figure 3, less reliable results were generated on the fish and mussel samples, particularly for the OC measurements, where recoveries from two biotic CRMs were only 24-79%. On the other hand, the analyses of coplanar PCBs 77, 81, 126 and 169 were very good, both in terms of accuracy and comparability. Figure 4 compares the interlaboratory coefficients of variation for coplanar PCBs in the standard solutions with those for the matrix samples.

### ***Toxaphene:***

The first toxaphene intercomparison (NCP II-4) confirmed that the different calibration standards being used made a significant contribution to the variability among laboratories, particularly for total toxaphene measurements. This can be seen in Figure 5 which clearly shows the bimodal distribution in these results. However, this Youden Pairs plot also shows that all participants had acceptable intralaboratory precision for their analyses of the two Hercules technical toxaphene standards. For the key biotic toxaphene congeners (Parlar 26, 38, 42, 44, ,50 and 62), good between-lab agreement was demonstrated by interlaboratory coefficients of variation of less than 25% for the blind congener solution and 18-49% for the burbot liver extract.





**Figure 3.** Accuracy and comparability of OC results in standard solutions (pg/ $\mu$ L) and biota samples (ng/g). Error bars represent the standard deviations of the interlaboratory results.

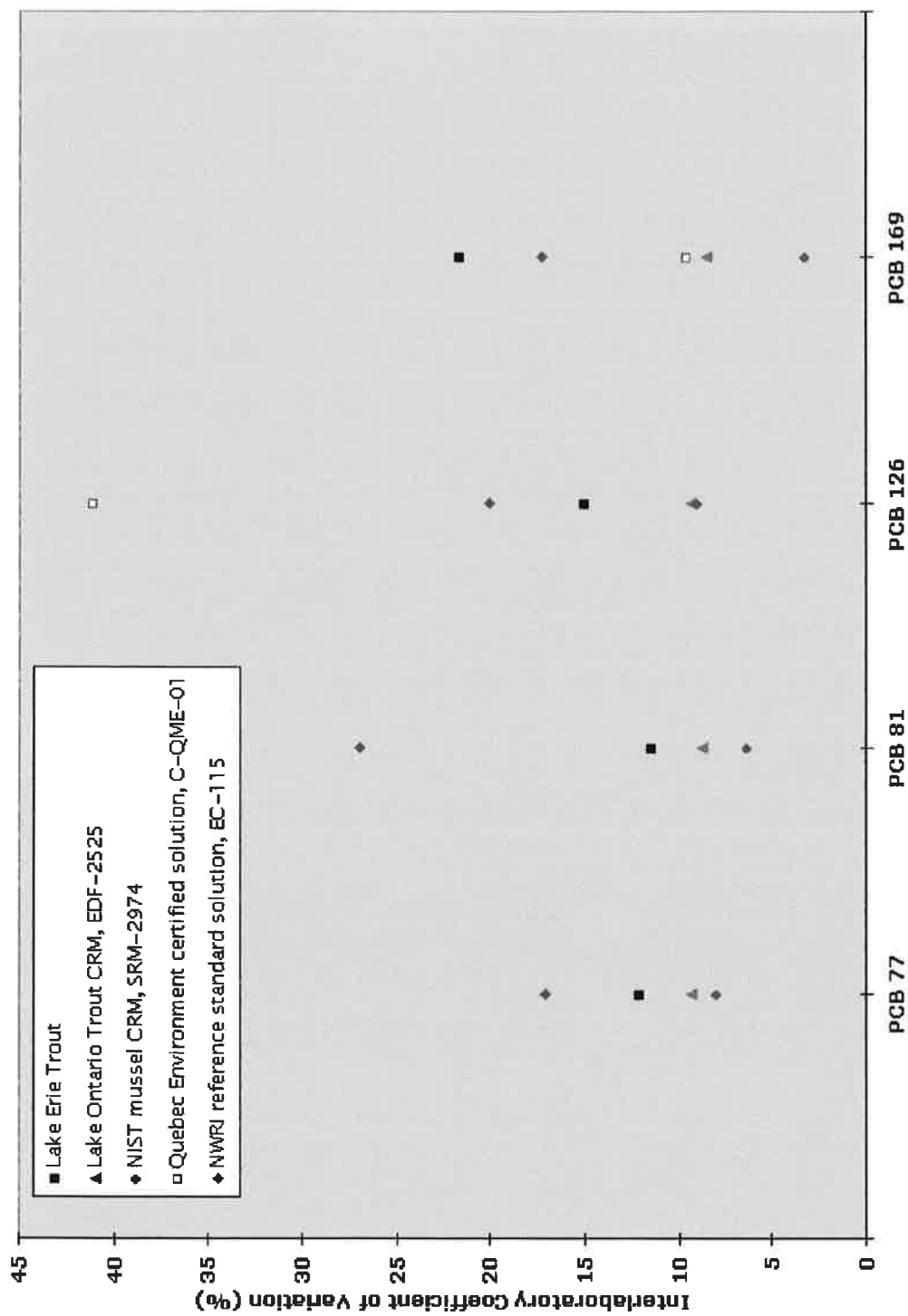
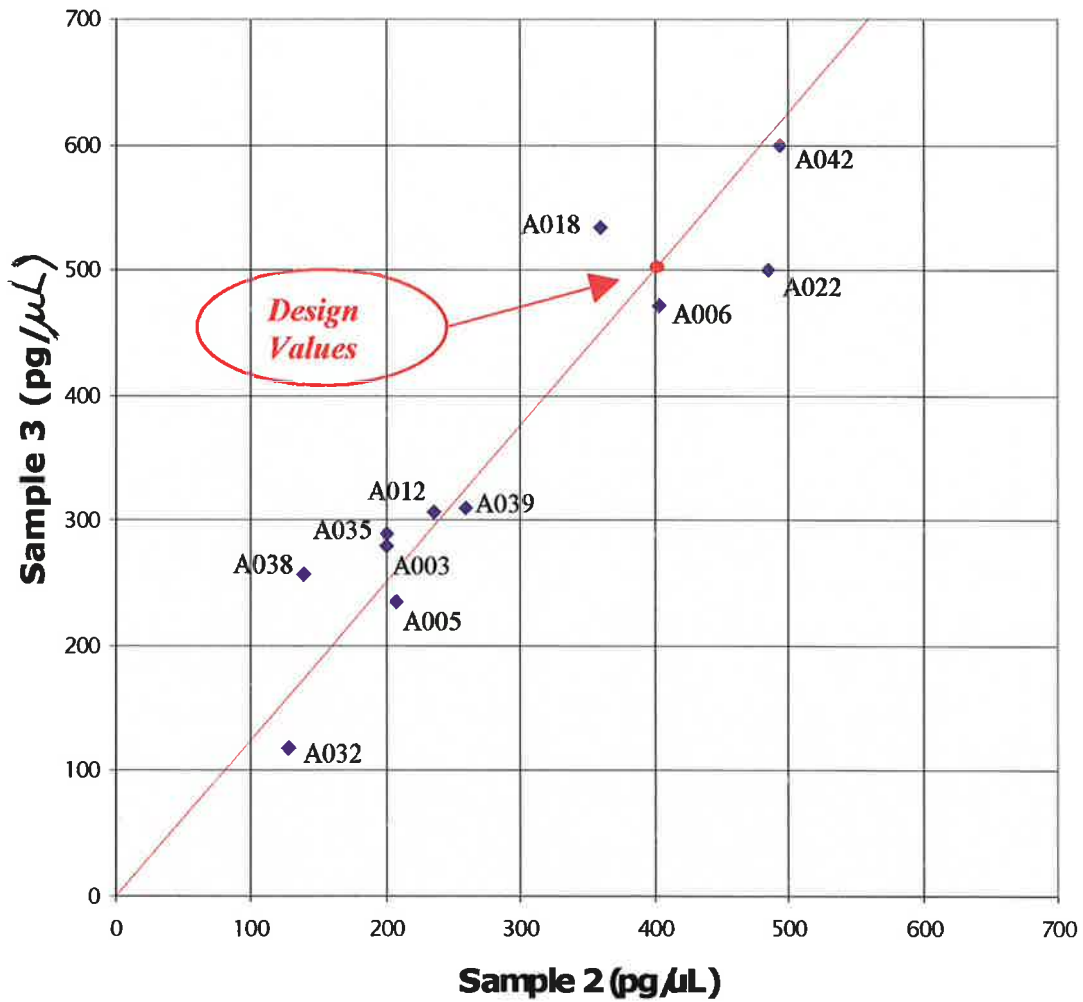


Figure 4. Interlaboratory comparability of coplanar PCB analyses in two standard solutions and three biotic samples.



**Figure 5.** Youden Pairs Plot of total toxaphene results for two Hercules standard solutions. The perpendicular closeness of each data point to the diagonal line demonstrates acceptable intralaboratory precision for all laboratories.

***Organotins:***

Measurements of monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) were accurate and comparable for the sediment samples, with some increased variability among laboratories shown for the standard solutions and biotic samples. In a blind assessment, the participants also demonstrated very good precision for their DBT analyses.

**CONCLUSION:**

Quality assurance and quality control are essential elements of all research and monitoring programs. Participation in the program provides NCP laboratories with a diagnostic tool for continual improvement in their measurement analyses. Furthermore, the results from these ongoing intercomparison studies provides assurance of the quality of NCP data being generated, both to the participating laboratories and to the science managers and decision makers of the NCP and its Regional Contaminants Committees. Finally, by offering a solid measure of assurance of the quality, reliability and intercomparability of NCP data, this QA program can also support the long-term objective of international scientific study and co-operation in Arctic research.

## REFERENCES

1. Stokker, Yvonne D. and Glynn Gomes. Summary Report of the Analytical Programs and Capabilities of Laboratories and Organizations that Contribute Measurement Data to the Northern Contaminants Program. (December 1998). NWRI Contribution No. 99-302.
2. Stokker, Yvonne D. and Glynn Gomes. Summary Report on the Availability and Suitability of External National and International Quality Assurance Programs Pertinent to the Northern Contaminants Program. (January 1999). NWRI Contribution No. 99-301.
3. Stokker, Y.D. Northern Contaminants Interlaboratory Quality Assurance Program. In S. Kalhok (ed.), *Synopsis of Research conducted under the 1998/99 Northern Contaminants Program*.
4. Stokker, Y.D. NCP Interlaboratory Quality Assurance Program for 1999-2000. In S. Kalhok (ed.), *Synopsis of Research conducted under the 1999/2000 Northern Contaminants Program*.
5. Stokker, Y.D. Northern Contaminants Interlaboratory QA Program for 2000-2001. In S.Kalhok (ed.), *Synopsis of Research conducted under the 2000/01 Northern Contaminants Program*.

Data summary reports are also available for each of the individual intercomparison studies.